



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: *Operando RIXS and HERFD-XAS on a Ni⁺/TiO₂/Ti³⁺ photocatalyst for noble metal- and sacrificial agent-free photocatalytic H₂ production*

Experiment number:
CH-6177

| | | |
|--------------------------|---|---------------------------------------|
| Beamline: ID26 | Date of experiment: from: 10 Nov 2021 to: 16 Nov 2021 | Date of report: 02 Mar 2022 |
| Shifts: 18 | Local contact(s): Viktoriia Saveleva | <i>Received at ESRF:</i> |

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Report:

Scope and experimental: Our aim was to confirm the formation of Ni(I) species and the dependence of the self-assembly process (described in the proposal) on the defective structure (Ti³⁺-O_v) of titania photocatalysts. For this, we performed in situ XAS measurements in fluorescence mode¹ for different TiO₂ photocatalysts, in aqueous suspensions in the presence of NiSO₄, with or without UV illumination. We recorded HERFD XAS spectra at the Ni-K edge. We studied three relevant photocatalysts: (i) “White” TiO₂, as received commercial anatase nanopowder; (ii) “Grey” TiO₂, i.e., “white” TiO₂ H₂-treated at 500°C; and (iii) “Black” TiO₂, i.e., “white” TiO₂ H₂-treated at 700°C. Darkening of TiO₂ upon hydrogenation confirms the formation of defective Ti³⁺-O_v structures in the oxide.

Results and discussion: We studied first the electrochemical reduction of a Ni(II) complex (Ni-cyclam) in an acetonitrile-based electrolyte, using an in situ XAS electrochemical cell. The XANES spectra at the Ni K-edge

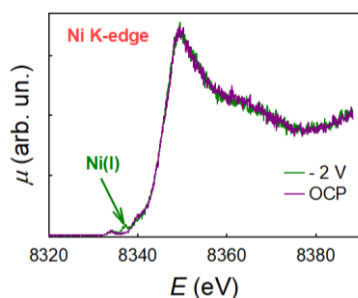


Figure 1 XANES spectra of the Ni-cyclam complex at OCP and -2 V.

of the Ni-cyclam complex are shown in the Fig. 1. We measured the spectra of the complex under open circuit potential (OCP) conditions, as a reference for Ni(II). When polarizing the working electrode at -2 V (vs. Ag), a new structure appears at ca. 8337 eV, as indicated by the green arrow in Fig. 1. We attribute this feature to the formation of Ni(I) species in the electrolyte.

We then performed in situ XAS experiments studying the different photocatalysts in suspensions, in the presence of Ni(II) ions, in the dark and under UV light illumination (i.e., under photocatalytic H₂ evolution conditions). The XANES spectra of “grey” TiO₂ are shown in Fig. 2. In the dark, the spectrum resembles that of Ni(II) hydrated ions. Upon illumination, a new broad feature appears at ca. 8337 eV, and this is indicative of the formation of Ni(I).

When the light is switched off, this structure decreases in intensity, thus confirming that the formation of Ni(I) is driven by illumination and is reversible. This correlates well with the high photocatalytic activity of “grey” TiO₂, as we observed in our previous work.²

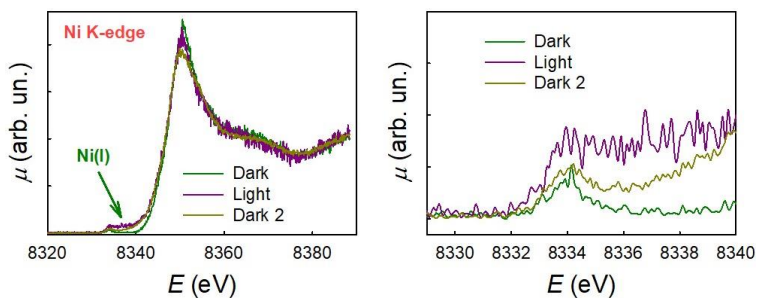


Figure 2 XANES spectra of “grey” TiO₂ in a 0.4 mM solution of NiSO₄ under intermittent UV light illumination.

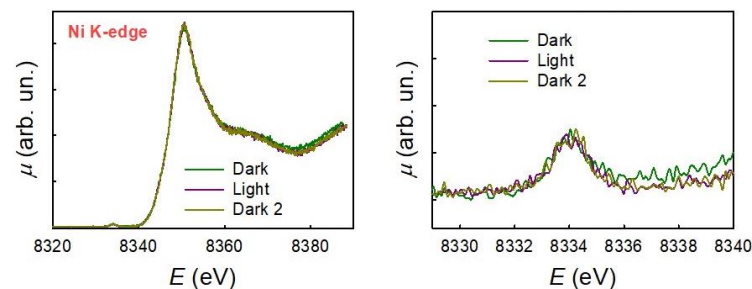


Figure 3 XANES spectra of “white” TiO₂ in a 0.4 mM solution of NiSO₄ under intermittent UV light illumination.

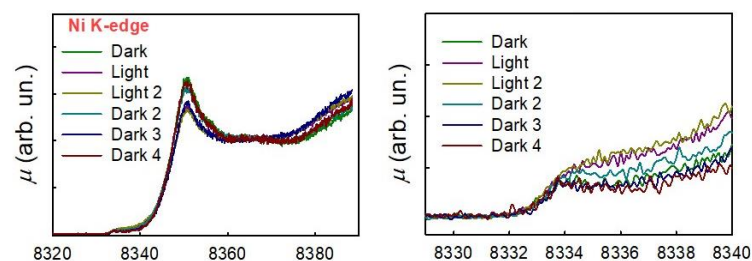


Figure 4 XANES spectra of “black” TiO₂ in a 0.4 mM solution of NiSO₄ under intermittent UV light illumination.

The XANES spectra at the Ni K-edge of “white” TiO₂ are shown in Fig. 3. In the dark, the spectrum resembles that of Ni(II) hydrated ions, and, under illumination, no differences can be detected. The same is valid for this sample in the dark after illumination. We, in fact, found in our previous work that “white” TiO₂ shows a negligible photocatalytic activity.²

The XANES spectra at the Ni K-edge of “black” TiO₂ are shown in Fig. 4. In the dark, the spectrum shows a spectral weight in the energy region of Ni(I), and this increases upon illumination. The original spectral shape is recovered after a long time in the dark (ca. 3 hours) after illumination. These conclusions are however made less straightforward by the fact that in the energy region characteristic of Ni(I), also Ni(0) has an increased spectral weight.

The results seem to indicate that defective Ti³⁺-O_v structures in “black” TiO₂ are highly reactive and form Ni(I) species also in the dark. This process, however, seem to be not reversible, or rather slow. Hence, Ni(I) surface species are highly stabilized and cannot therefore significantly contribute to the H₂ evolution reaction. Note that, in fact, “black” TiO₂ shows a negligible photocatalytic activity, as found in our previous work.²

Conclusions: In situ XAS results provided solid evidence that:

- Ni(I) species, which form on “grey” TiO₂ but not on “white” TiO₂, catalyze photocatalytic H₂ evolution (proton reduction) in the absence of a sacrificial agent and noble metal co-catalyst.
- The formation of Ni(I) species is dependent on the presence in the TiO₂ nanoparticles of surface Ti(III) sites, thus creating an artificial redox chain based on a monovalent nickel (Ni(I)) electron transfer relay. Thus, the formation of surface Ni(I) species is the rate determining step in the H₂ evolution process.
- Different H₂ treatments (different temperatures) form defective Ti³⁺-O_v structures in the oxide that have different density, distribution, and energy,³ in line with recent in situ EPR studies.⁴
- Defective Ti³⁺-O_v structures in “black” TiO₂ are highly reactive and form Ni(I) species also in the dark. This process, however, is not reversible, indicating that Ni(I) surface species are highly stabilized and cannot therefore contribute to the H₂ evolution reaction.

Our findings are important as we unequivocally demonstrate that using defective titania allows for the in-situ activation of a self-amplifying photocatalytic system that generates H₂ from an aqueous Ni²⁺ solution. No deposition of metallic Ni or other co-catalytic Ni-compounds could be detected. No hole scavengers are required. Rather, the in-situ activation process couples surface structural defects on TiO₂ with the formation of single valent Ni(I) species that are able to rapidly reduce protons to H₂. Self-amplifying reaction schemes as observed in this experiment may have a considerable potential for simple one pot synthesis and use of photocatalysts. We are currently preparing an article featuring the XAS data compiled in this report.

References:

- 1 D. Spanu, A. Minguzzi, S. Recchia, F. Shahvardanfard, O. Tomanec, R. Zboril, P. Schmuki, P. Ghigna and M. Altomare, *ACS Catal.*, 2020, **10**, 8293–8302.
- 2 S. Qin, Z. Badura, N. Denisov, O. Tomanec, S. Mohajernia, N. Liu, S. Kment, G. Zoppellaro and P. Schmuki, *Electrochem. commun.*, 2021, **122**, 106909.
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- 4 Z. Bad'ura, A. Naldoni, S. Qin, A. Bakandritsos, Š. Kment, P. Schmuki and G. Zoppellaro, *ChemSusChem*, 2021, **14**, 4408–4414.